OVERVIEW: CHEESE CHEMISTRY AND RHEOLOGY

V. H. Holsinger, Philip W. Smith, and Michael H. Tunick

Eastern Regional Research Center
Agricultural Research Service
United States Department of Agriculture
Philadelphia, PA 19118

INTRODUCTION

Cheese is the generic name of a group of cultured fermented products represented world-wide in well over 500 varieties. More than 700 varieties are described in USDA Handbook No. 54 (Walter and Hargrove, 1969). Cheese represents perhaps one of the oldest means of food preservation and is made wherever animals are milked, whether the animal is a cow, buffalo, reindeer, goat, sheep, horse, camel, ass, yak or llama. Cheese is highly nutritious because it contains almost all of the protein, usually most of the fat, essential vitamins and minerals and other nutrients of milk in a concentrated form.

HISTORY

Historians believe that cheese originated in the Tigris-Euphrates Valley over 8000 years ago in what is now Iraq. At some stage, man recognized the nutritive value of milk and began to consume it along with the baby animal. However, because milk is such a fine growth medium, it would quickly sour and coagulate in warm climates through production of lactic acid by the contaminating microorganisms. When it was discovered that if the clot were broken up, the whey could be consumed immediately while the curd was preserved, by heavy salting, by air drying or by a combination of the two, cheesemaking was born. Lactic acid, therefore, appears to be the first milk coagulant.

It also became clear at an early stage, that something in animal stomach would cause milk to coagulate. Storage of milk in bags made from stomach was common and is still in use in many countries today.

The history of cheesemaking has been reviewed and the reader is referred to the literature for more details (Fox, 1993; Scott, 1986). Cheesemaking accompanied civilization's spread throughout the Middle East, Greece and Rome. Biblical references and classical Greek and Roman literature all refer to cheesemaking. At its height, cheese was made in many parts of the Roman Empire and was a standard army ration; the Romans are credited with introducing cheesemaking into Great Britain. During the Middle Ages, cheese was made and improved mainly by the great monasteries and feudal estates of Europe. Gorganzola was made in the Po Valley in Italy in 879 A.D.; in the 10th century, Italy was the cheesemaking center of Europe (Walter and Hargrove, 1969). Many popular cheese varieties today, such as St. Paulin, Wensleydale, Port du Salut, and Trappist, for example, were developed in the monasteries; Roquefort is mentioned in the records of the monastery at Conques, France, in 1070. Cheese was included in the ship's supplies when the Mayflower sailed for the New World in 1620.

Until the middle of the 19th century, cheesemaking remained an art form, handed down from generation to generation. Although many happy accidents led to the development of the several hundred distinct varieties, there were many failures as well. The first cheese factory in the United States was built near Rome, New York, by Jesse Williams. Herkimer County, New York, became the center of the cheese industry in the United States for the next 50 years. With expanding population in the East, the industry gradually moved westward, finally centering in the farm regions of Wisconsin.

Today, cheese is primarily a product of European countries and of those populated by European emigrants. Where diets are based more on plant products and where no dairying tradition exists, cheese is of relatively little importance.

CHEESE MANUFACTURING

In contrast to most dairy products, cheese represents a dynamic biological system: throughout the manufacturing and ripening process, a series of concurrent and/or successive biochemical events occur, that, if balanced, yield a product of desirable flavor, odor and texture. No two cheeses are ever identical, even batches of the same variety.

The vast variety of cheeses can be divided into manufacturing and ripening phases. Fox (1993) defines the manufacturing stage as those events that occur during the first 24 hours; much of the following discussion is taken from his review. Basic steps are: acidification; coagulation; dehydration (cutting, cooking, stirring, pressing, salting); shaping (molding, pressing); and salting.

Cheesemaking is basically a dehydration process whereby the fat and casein are concentrated six to twelve times, depending on the cheese variety. The amount of water retained in the product is regulated by the extent and combination of the five steps listed above plus the milk's composition. The biochemical changes during the subsequent ripening period are regulated by the moisture content, the salt content and the microflora. These factors, in turn, lead to the flavor, odor and texture of the finished product.

Acidification

The first and most basic operation, acidification, is defined as the progressive development of acidity throughout the manufacturing stage, and, for some varieties, in the early stages of ripening as well. Acid production is the key to the production of good quality cheese. It affects coagulant activity, curd strength, syneresis, pH and growth of non-starter microorganisms.

Coagulant activity and the amount of coagulant retained in the curd affect the rate of proteolysis during ripening. The curd strength affects the yield; if the curd is too fragile, it shatters, leading to significant losses of fat and protein in the whey. Syneresis controls the moisture content which regulates bacterial growth and enzyme activity, which, in turn, influence the rate and pattern of ripening. The pH affects the rate of solubilization of the colloidal calcium phosphate, which affects casein susceptibility to proteolysis and influences the rheological properties of the cheese. If it is too acid, the cheese is crumbly; if too basic, the cheese is pasty and sticky. Finally, the growth of many non-starter microorganisms, especially food poisoning and gas producing ones, is controlled by the lactic-starter organisms; as a result, properly made cheese is inherently a very safe product.

Coagulation

The second step in the manufacturing process is coagulation: the milk forms a gel that entraps the fat. Coagulation is achieved in three ways: by limited proteolysis by selected aspartate proteinases, usually chymosin (rennet), acidification to the isoelectric point of casein of approximately pH 4.6, or acidification to about pH 5.2 with heating.

Rennet coagulation has become predominant in modern cheese-making. The properties of rennet curds are quite different from those of acid precipitated curds in that they have better syneresis properties that make it possible to produce low moisture curd without hardening. For several thousand years, rennets from the stomachs of young animals were the standard and are still regarded as the best coagulants, although shortages have made it necessary to obtain proteinases from fungal or microbial sources (acid proteinases from *Mucor meihei* or *Endothia parasitica*) or use rennet substitutes (usually bovine or porcine pepsin). The newest rennet substitutes, fermentation-derived chymosins, are expressed in varieties of *Aspergillus niger, Kluveromyces marxianus,* and *Escherichia coli* (Farkye, Chapter 11). Coagulating agents from some plants may also be used. Reviews on milk clotting enzymes and rennet substitutes are available (for example, Brown and Ernstrom, 1988; Foltmann, 1993).

Rennet coagulation occurs in two phases: an enzymatic phase where the Phe105-Met106 bond of kappa-casein is hydrolyzed to release the hydrophilic glycomacropeptide from the C-terminal end. This occurs down to a temperature of 0°C. However, for the coagulum to form in the second phase, the temperature must be greater than 18°C. The enzymatic hydrolysis destabilizes the casein micelle in the presence of a critical concentration of calcium ion to form a gel. This unique behavior has been extensively researched (Dalgleish, 1993; Green and Grandison, 1993).

Dehydration (Post-Coagulation Changes)

The post-coagulation changes are those that determine the quality of the finished cheese. The rennet gel is very stable if it is quiescent, but it quickly synereses when cut, expelling the whey. The rate and extent of syneresis are controlled by the milk composition, especially the calcium ion concentration, the pH of the whey, the temperature of cooking, the rate at which the curd is stirred with the whey and time. It is at this point that differentiation into the different cheese varieties really begins, although the amount and type of starter culture and coagulant and composition of the cheese milk are certainly significant.

Each variety of cheese has its own manufacturing schedule. A sample schedule for Cheddar cheese is shown in Table 1. Although the time shown is only seven hours, it takes additional time to pasteurize and standardize the milk, heat it to the desired temperature and ripen the milk, if desired, before starter addition.

Salting

Salting does not control the amount of moisture in the cheese even though it does affect syneresis. Salt has several important functions in cheese. Although salting during cheese manufacture appears to be easy, if it is done incorrectly, adverse effects on cheese quality occur.

Salt has its greatest role in ripening where it controls water activity, microbial growth and activity, enzyme activity and physical changes in the cheese proteins that influence

Table 1. Manufacture of Cheddar cheese.

Step	Time		
Add starter			
Add rennet (setting)	1 hr		
Cutting	20-30 min		
Steam on	15 min		
Steam off	30 min	2 hr, 15 min	4 hr, 30 min
Drain whey (dipping)	15 min	2 hr, 15 min	7 hr
Packing			
Milling	15 min		
Salting	30 min		
Hooping			
Pressing	30 min		
Dressing			

texture and solubility through possible changes in protein conformation.

RIPENING

Space does not permit a review all of the biochemical changes that occur in cheese during ripening. Such changes include glycolysis, lipolysis and proteolysis. Secondary catabolic changes also occur, such as deamination, decarboxylation, beta-oxidation, and even ester formation. However, proteolysis is considered by most researchers to be the principal ripening reaction; this has been related to rheological properties as described in later chapters in this volume.

Detailed discussions of the specific aspects of ripening of the major cheese varieties (Cheddar, Dutch, Swiss, Italian, etc.) are in Fox (1987); a general overview of the biochemistry of ripening has been described by Fox, et al. (1993).

Most cheeses coagulated by acid alone or by heat and acid are unripened. The milk coagulates at the isoelectric point, around pH 4.6. Typical compositions of fresh cheeses are listed in Table 2. Cottage cheese is the fresh variety of cheese familiar to most people

Table 2. Percent composition of typical fresh cheeses.

Component	Creamed Cottage	Cream	Quarg
Water	79	54	79
Fat	4.5	34.8	0.2
Protein	12.5	7.6	15.0
Salt	1.03	0.75	0.7
Carbohydrate	2.7	2.7	____
Ash	1.4	1.2	____

Source: Posati and Orr (1976)

in the United States. Other examples include Bakers' cheese, cream cheese, Queso Blanco, Neufchatel and Quarg, especially popular in Europe. As shown in Table 2, all these examples of fresh cheese are high in moisture, although fat content varies widely. They are designed to be consumed within a short time after their manufacture.

CLASSIFICATION OF CHEESE

The principal varieties of cheese may be produced in several different countries. Many schemes have been proposed for the purpose of classifying cheeses to make them as standard as possible for international trade purposes. Schemes based on manufacturing parameters, chemical fingerprints, moisture content, rheological parameters or coagulating agent have been developed but none has been fully satisfactory (Fox, 1993; Scott, 1986). With the development of sophisticated rheological testing devices, new directions in predicting user assessment of cheese properties may be possible.

Rheology

The first rheological measurements of cheese were empirical: the cheese grader would press the surface with a thumb to judge firmness and elasticity. Davis (1965) was the first to perform fundamental rheological studies of cheese when he compressed cylinders of four English types under a constant load. These force-deformation tests were the forerunners of much of the recent cheese rheology research. Davis' classification scheme was based on viscosity, elasticity, and springiness logarithmic factors. He divided his cheese types into four categories related to the moisture content. Although this scheme appeared satisfactory for rennet cheeses, it was not applicable to high moisture soft fresh cheeses. Scott Blair and associates (1949) have performed much fundamental work on cheese and other foods, emphasizing the viscoelastic properties; their work has led to an increase in the application of rheological theory to food analysis. Testing methods and cheese rheology have been reviewed recently (Tunick and Nolan, 1992; Konstance and Holsinger, 1992).

Texture profile analysis by Instron* testing machine and small amplitude oscillatory shear have been used to study the viscoelastic properties of various cheeses. Dynamic testing offers a very rapid test with minimal chemical and physical changes in the sample. Mechanical properties such as Young's modulus may be determined at various frequencies and temperatures within a short time. Another advantage of dynamic testing is the extremely small strains, usually within one per cent, imposed on the sample, assuring a linear stress-strain behavior. Small strains are vital to the use of viscoelastic models in predicting behavior.

Nolan et al. (1989) studied the properties of low moisture part skim Mozzarella cheese, both natural and imitation, with a Rheometrics RDA Model 700 Dynamic Analyzer in a parallel plate configuration. Imitation cheeses were made by adding one or two per cent of calcium caseinate by weight of fluid milk before pasteurization. Viscosity proved sensitive to added caseinate; a fifty per cent increase in viscosity was observed at room temperature with two per cent added caseinate.

The viscoelastic shear modulus is frequency dependent. As shown in Table 3, at one per cent added calcium caseinate, the elastic and viscous components of the shear modulus were increased over those of the corresponding values of the control Mozzarella. However, at the two per cent level, the G' (elastic modulus) decreased below the baseline

---

Table 3. Shear moduli of natural and imitation Mozzarella cheese.

Sample	Elastic component G′ (dyn/cm^2)	Viscous component G″ (dyn/cm^2)
Mozzarella	$2.27 \times 10^5\omega^{0.17}$	$1.03 \times 10^5\omega^{0.19}$
1% Calcium caseinate	$5.92 \times 10^5\omega^{0.20}$	$1.98 \times 10^5\omega^{0.14}$
2% Calcium caseinate	$1.59 \times 10^5\omega^{0.21}$	$1.98 \times 10^5\omega^{0.16}$

ω = radians/sec
Data were obtained at 0.5% strain with a 4 mm gap.
Source: Nolan et al. (1989)

value, but the viscous component (G″) increased. This finding was not explained but with the report by Tunick, et al. (1989) that the distribution of the fat globules was not uniform in the imitation cheese, the viscoelastic modulus may be affected by the nonuniform distribution of the milkfat.

This is only one example of the application of this sophisticated technique to evaluate some of the physical properties of cheese. Rheological testing provides greater insight into the effects of varying composition and processing on texture and can aid in the development of novel cheese products.

REFERENCES

Brown, R.J., and Ernstrom, C.A., 1988, Milk-clotting enzymes and cheese chemistry, Part I—milk clotting enzymes, *in*: "Fundamentals of Dairy Chemistry," N.P. Wong, ed., 3rd Ed., Van Nostrand Reinhold Co., New York, p. 609.

Dalgleish, D.G., 1993, The enzymatic coagulation of milk, *in*: "Cheese: Chemistry, Physics and Microbiology," P.F. Fox, ed., Vol. I, 2nd ed., Chapman and Hall, London, p. 69.

Davis, J.G., 1965, "Cheese: Basic Technology," Vol. I, Churchill Livingstone, London.

Foltmann, B., 1993, General and molecular aspects of rennets, *in:* "Cheese: Chemistry, Physics and Microbiology," P.F. Fox, ed., Vol I, 2nd Ed., Chapman and Hall, London, p. 37.

Fox, P.F., 1993, Cheese: an overview, *in:* "Cheese: Chemistry, Physics and Microbiology," P.F. Fox, ed., Vol. I, 2nd Ed., Chapman and Hall, London, p. 1.

Fox, P.F., ed., 1987, "Cheese: Chemistry, Physics and Microbiology," Vol. 2, Major Cheese Groups, Elsevier Applied Science Publ., London.

Fox, P.F., Law, J., McSweeney, P.L.H, and Wallace, J., 1993, Biochemistry of cheese ripening, *in:* "Cheese: Chemistry, Physics and Microbiology," P.F. Fox, ed., Vol. I, 2nd Ed., p. 389.

Green, M.L., and Grandison, A.S., 1993, Secondary (non-enzymatic) phase of rennet coagulation and post-coagulation phenomena, *in:* "Cheese: Chemistry, Physics and Microbiology," P.F. Fox, ed., Vol. I, 2nd Ed., Chapman and Hall, London, p. 101.

Konstance, R.P. and Holsinger, V.H., 1992, Development of rheological test methods for cheese, *Food Technol.* 46:105.

Nolan, E.J., Holsinger, V.H. and Shieh, J.J., 1989, Dynamic rheological properties of natural and imitation Mozzarella cheese, *J. Text. Stud.* 20:179.

Posati, L.P. and Orr, M.L., 1976, "Composition of Foods: Dairy and Egg Products: Raw - Processed - Prepared," U.S. Department of Agriculture Handbook No. 8-1, Washington, D.C.

Scott, R., 1986, "Cheesemaking Practice," 2nd Ed., Elsevier Applied Science Publ., London, p. 1.

Scott Blair, G.W. and Baron, M., 1949, The rheology of cheese making, *in:* Proc. of 12th Intern. Dairy Cong., Vol. 2, p. 49.

Tunick, M.H. and Nolan, E.J., Rheology of cheese, *in:* "Physical Chemistry of Food Processes," I.C. Baianu, ed., Vol. I, Fundamental Aspects, Van Nostrand Reinhold Co., New York, p. 273.

Walter, H.E. and Hargrove, R.C., ed., 1969, "Cheese Varieties and Descriptions," U.S. Department of Agriculture Handbook No. 54, Washington, D.C.